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Chemical ionization mass spectrometry of $Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$; a new approach to gas phase reactivity

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Abstract

The gas phase reactivity of the title compounds has been investigated by chemical ionization mass spectrometry. The reaction pathways are deduced by plotting the relative ion abundances versus the reactant gas pressure. The information gained with this new approach is compared with the available data by ICR. The pentacoordinated and polynuclear species observed are discussed with regard to their formation in the condensed phase.

Introduction

Although ion cyclotron mass spectrometry (ICR) is the best method to investigate the gas phase ion reactivity, the conventional chemical ionization mass spectrometry (CIMS) is a useful and rapid technique to get information on the overall behaviour of ions in the gaseous phase.

In recent years transition metal nitrosyl compounds have attracted considerable interest [1] for the unusual bonding ability of this ligand; following our previous studies [2], we have investigated the gaseous phase reactivity of two simple tetrahedral compounds, $Fe(CO)_2(NO)_2$ (**I**) and $Co(CO)_3NO$ (**II**), with the goal to seek for the formation of pentacoordinated species since an increase in the coordination number has been invoked in some substitution reactions in the condensed phase [3], and to seek for unusual compounds in view of the extensive occurrence of ligand substitution reactions involving both σ- and π-bonding ligands.

The use of labelled gases and, mainly, the influence of the reacting gas pressure on the relative abundances of the metal containing ions seem useful tools to get information on their formation paths, even if this technique cannot replace ICR mass spectrometry which remains the only means capable of securely identifying mechanisms involving single ionic species.

Experimental

The title compounds were prepared according to published procedures [4]. Mass spectra were obtained with a Finnigan Mat 112S mass spectrometer equipped with a chemical ionization ion source. The reactant gases were reagent grade products and their pressure in the ionization box was kept between 1 and 100 Pa. The pressure measuring device consists of a tube, gas-tight coupled to the ionization box, bearing a Pirani gauge-head. Depending on the reagent gas, significant variations in the mass spectra were observed in the 1–20 Pa range. Mass spectra presented in this work have been obtained at 40 Pa with the exception of the data relative to C_2D_2 reactant gas. The ion source temperature was 140 °C and the electron energy was 100 eV.

Results and discussion

Electron impact mass spectra

While the mass spectra of the two compounds recorded at normal conditions are in close agreement with previous reports [5], an increase of the pressure of the samples in the ion source (using the chemical ionization box) leads to the formation of several polynuclear species (Fig. 1). The ability to undergo clustering reactions had already been fully reported for $Co(CO)_3NO$ [6] but information was not available for the iron compound. We find a substantial agreement in the nature of the species observed by ICR and by EI for compound **II**; the mass spectrum is

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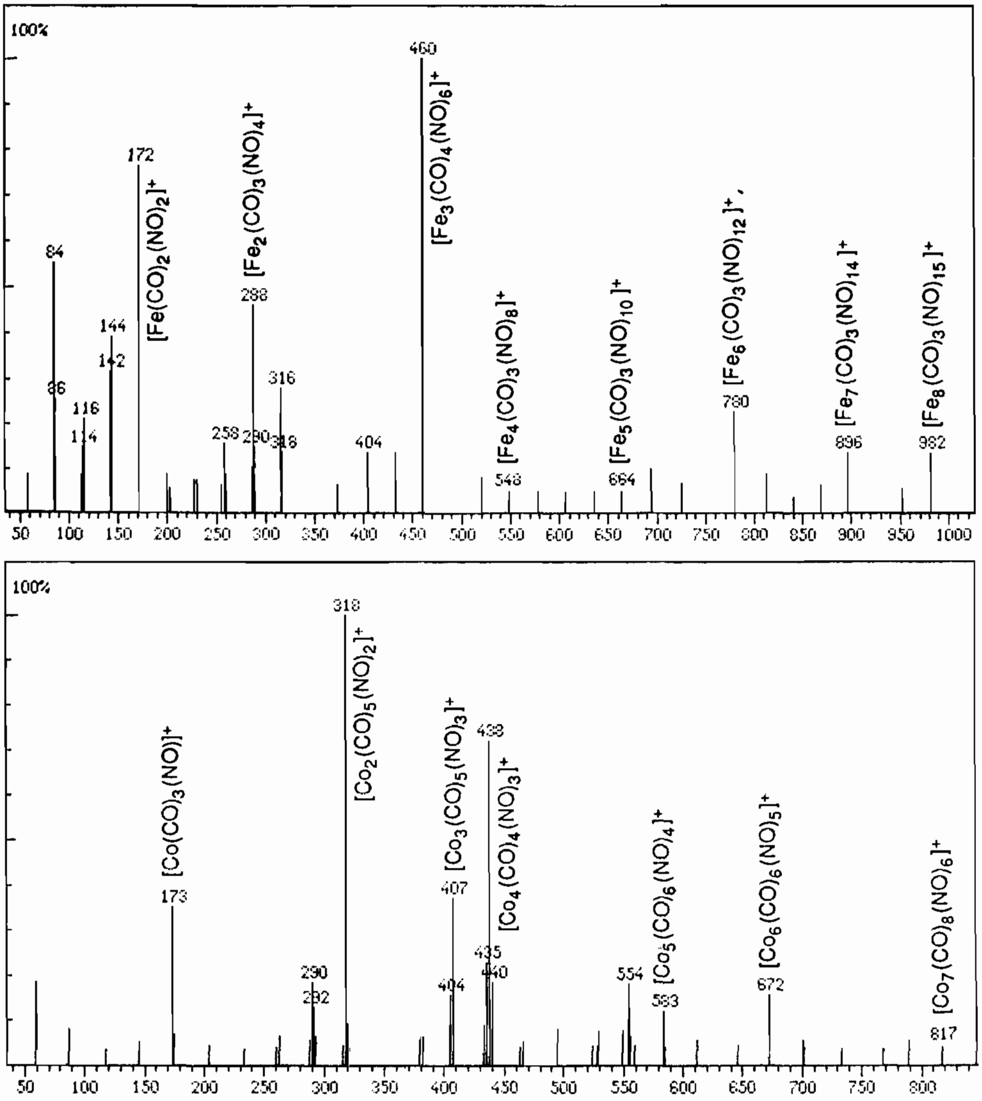

Fig. 1. Mass spectra of $Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$ at 10 Pa sample pressure.

strongly influenced by the sample pressure but the ion 318, probably formed according to the reaction

$$Co(CO)_3NO + [Co(CO)_3NO]^+ = [Co_2(CO)_5(NO)_2]^+ + CO$$

is always among the more intense peaks.

Also compound **I** exhibits the usual strong tendency for clustering reactions [7a, b, c] and species with up to 8 metal atoms were observed.

Hydrogen and methane CI mass spectra

Table 1 reports the mass spectra of **I** and **II**. When the reagent gas is H_2, the molecular ion is observed with high abundance; this ion is formed by a charge exchange reaction; this process is accompanied by proton transfer reaction which is the main process when the reagent gas is methane. The lack of any specific fragmentation pathway of the protonated molecule prevents drawing any conclusion concerning the protonation site.

Figures 2 and 3 show the influence of the reacting gas pressure on the relative abundances of the main metal-containing ions. The marked difference between the ion abundances at low and high pressure is due to the variation of the relative abundance of different reacting ions in the gases. With H_2 as reagent gas at low pressure the main ion present is H_2^+ which reacts by charge exchange and induces high fragmentation because of its high recombination energy ($RE = 15.4$ eV) compared with the ionization energy of compounds **I** and **II** [8]; increasing the gas pressure the ion H_3^+ becomes more abundant

TABLE 1. Hydrogen and methane chemical ionization mass spectra of iron and cobalt complexes

Ions	$Fe(CO)_2(NO)_2$ (reagent gas)		$Co(CO)_3(NO)$ (reagent gas)	
	H_2	CH_4	H_2	CH_4
$[M_2-CO+H]^+$		3		6
$[M_2-CO]^+$	31	1	14	1
$[M-2CO+H]^+$	17	2	38	8
$[M-2CO]^+$	18	1	24	2
$[M_2-3CO+H]^+$	21	1	21	1
$[M_2-3CO]^+$			10	1
$[M_2-4CO+H]^+$	27		5	
$[M+(C_3H_5)]^+$		1		<1
$[M+(C_2H_5)]^+$		2		<1
$[M+(CH_3)]^+$		4		1
$[M-CO+(C_3H_5)]^+$		3		1
$[M+H]^+$	53	100	60	100
$[M]^+$	46	3	46	4
$[M-2CO+(C_3H_5)]^+$		5		11
$[M-CO+H]^+$	100	8	100	17
$[M-CO]^+$	13	2	11	2
$[M-2CO+H]^+$	18		10	
$[M-2CO]^+$	7			
$[M-CO-NO]^+$	8			
$[M-2CO-NO]^+$			6	
[Fe, Co]$^+$	11		12	

M = molecular formula.

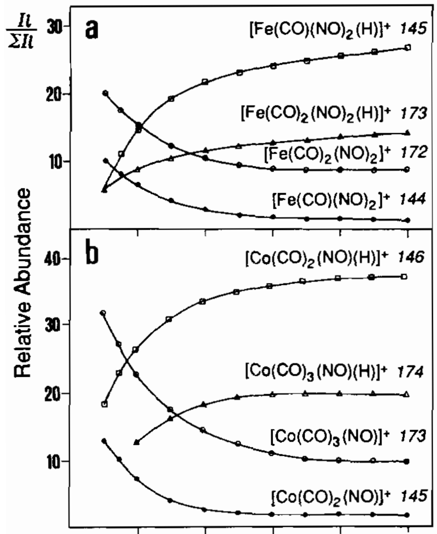

Fig. 2. Abundance vs. hydrogen gas pressure for selected ions of $Fe(CO)_2(NO)_2$ (a) and $Co(CO)_3(NO)$ (b).

so that the protonated molecule and its fragment increase; the charge exchange reaction is still present but the lower *RE* of H_3^+ (9.3 eV) reduces the fragmentation reactions of the molecular ion.

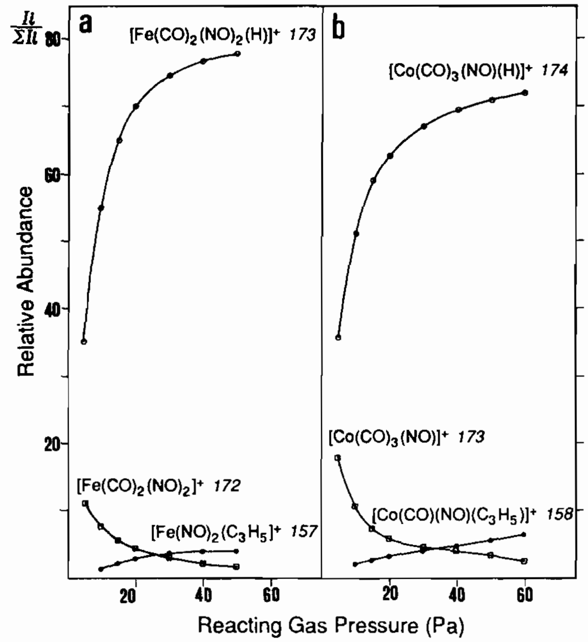

Fig. 3. Abundance vs. methane gas pressure for selected ions of $Fe(CO)_2(NO)_2$ (a) and $Co(CO)_3(NO)$ (b).

The methane system offers more simple spectra since the charge exchange reaction is reduced* (*RE* for this system is between 8 and 8.4 eV) and the fragmentation of the protonated molecule is reduced because of the lower energy transfer resulting from the higher proton affinity of CH_4 compared to that of H_2.

The presence of other reactive ions leads to new reactions when methane is the reactant gas; the more prominent of these ions, $C_3H_5^+$, gives rise to carbonyl substitution reactions and, to a lower extent, also to addition reactions; a different behaviour was observed by ICR where only the ion $Co(CO)(NO)(C_3H_5)^+$ is present [9].

The plots of Fig. 2(a) are an example of the ability of this technique to give information on the reaction pathways. The parallel behaviour of the 173 and 145 ions whose relative abundance increases with the reactant gas pressure, and the reverse behaviour of the 172 and 144 ions, indicate that the 145 ion is formed by fragmentation of the protonated molecule and is not due to a reaction of the 144 ion with the reactant gas. Dimeric species are more abundant when the reactant gas is hydrogen (see Table 1); this indicates that dimer formation is promoted by coordinatively unsaturated ions which are more abun-

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*The abundance of the molecular ion is greater at low gas pressure and might be due to some charge exchange with the CH_4^+ ion, whose abundance sharply decreases with the methane pressure.

dant with this system gas which transfers more energy to the molecular ion or to the protonated molecule; the greater reactivity of these fragment ions has already been reported [6]. Scheme 1 summarizes the major reactions observed with these gases; in this scheme the reactions of the ion $C_3H_5^+$, leading to low abundance ions, are not supported by the observation of pressure effects. The formation of the ion 158 is suggested as a primary reaction, in agreement with the reported ICR results; no indication is available for the formation of the ion 186; the reactions of compound **I** with the ion $C_3H_5^+$ are only tentative. Low abundance ions due to methyl and ethyl addition are also observed and are not reported in Scheme 1.

Ethylene mass spectra

Ethylene is a complex reacting system with several ions whose relative abundance is strongly dependent upon pressure as shown in Fig. 4; in addition the nominal mass of CO and C_2H_4 is the same and the mass difference among couples of possible reactive ions is 28 u. In these conditions the use of ethylene prevents a correct ion assignment, so that we used ethylene-d_4 (which gives an identical reacting system) to discriminate among the various reactions. From Fig. 4 it is evident that at pressures greater than 20 Pa about 80% of the total ion current is due to the ion $C_5H_9^+$; since at these pressures the abundance of the CI mass spectra of **I** and **II** is strongly reduced, we suggest that this last ion has a limited reactivity towards the two substrates. Table 2 reports the mass spectra of **I** and **II** obtained by using the two reacting gases; it is evident that several ions of the same nominal mass show up a different structure when the deutero derivative is used.

Figure 5 shows the variation of the major ion abundances with the ethylene-d_4 pressure for compound **I**; the trends of the ions abundances versus the gas pressure suggest the following reactive behaviour (see Scheme 2).

(a) Reactions with $C_2D_4^+$

This ion is able to undergo charge exchange reaction followed by a reduced fragmentation up to the first carbonyl loss*. The relative abundance of these ions sharply decreases increasing the gas pressure, probably because they react with the neutral

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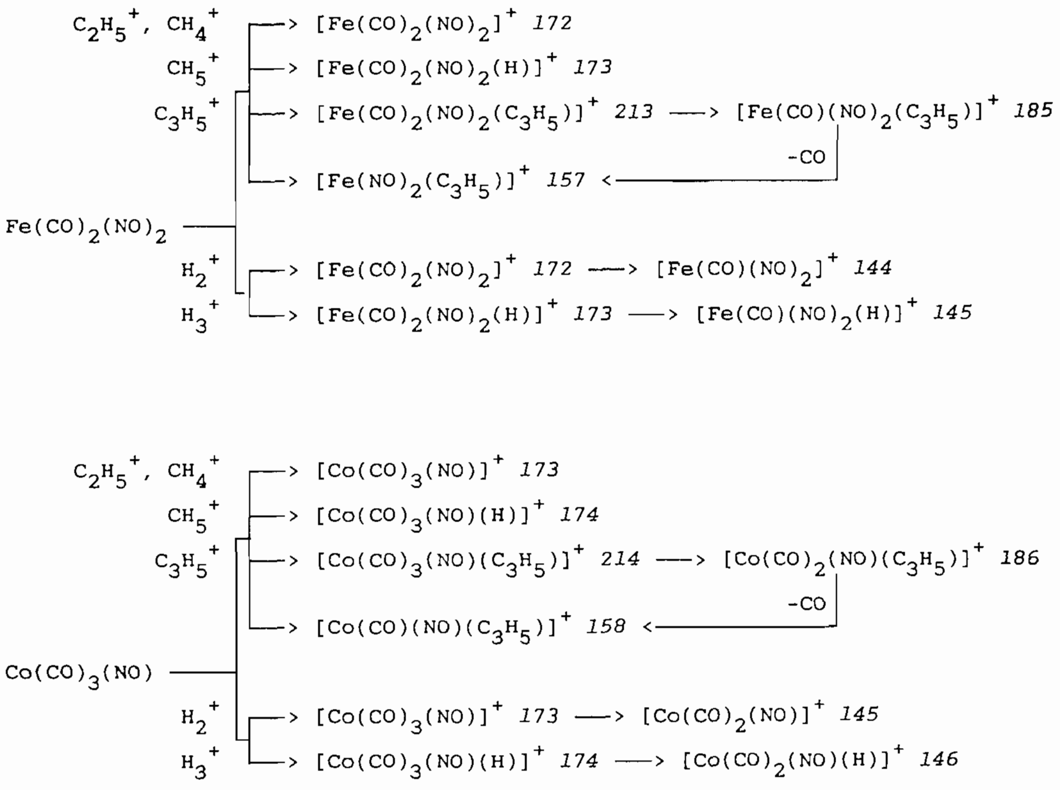
*Unpublished results from this laboratory indicate that the energy supplied by the reactant ion can only lead to the loss of one CO group.



Scheme 1.

TABLE 2. Ethylene and ethylene-d_4 (30 Pa) chemical ionization mass spectra of iron and cobalt complexes

Ions	$Fe(CO)_2(NO)_2$ (reagent gas (C_2X_4))		$Co(CO)_3(NO)$ (reagent gas (C_2X_4))	
	X=H	X=D	X=H	X=D
$[M-CO+(C_5X_9)]^+$	11	8	6	1
$[M+(C_2X_5)]^+$	7	10	6	2
$[M-3(CO)+(C_2X_4)_2+(C_3X_5)]^+$			7	9
$[M-2CO+(C_3X_5)+(C_2X_4)]^+$	36	35		8
$[M-2CO+(C_5X_9)]^+$				
$[M-CO+(C_3X_5)]^+$		5		1
$[M-2CO+(C_2X_5)+(C_2X_4)]^+$	16	6	30	13
$[M-CO+(C_2X_5)]^+$		10		12
$[M+(X)]^+$		12		15
$[M]^+$	100	6	100	9
$[M-CO+(C_2X_4)]^+$		70		100
$[M-2CO+(C_2X_4)_2]^+$		100		16
$[M-3CO+(C_2X_4)_3]^+$				16
$[M-2CO+(C_3X_5)]^+$	2	4	68	30
$[M-3CO+(C_3X_5)+(C_2X_4)]^+$				29
$[M-CO+(X)]^+$	4	1	3	1
$[M-2CO+(C_2X_5)]^+$		5		5
$[M-2CO+(C_2X_4)]^+$	4	7	87	6
$[M-3CO+(C_2X_4)_2]^+$				95

M=molecular formula; the square brackets contain the total ion intensity of different assignments with same nominal mass.

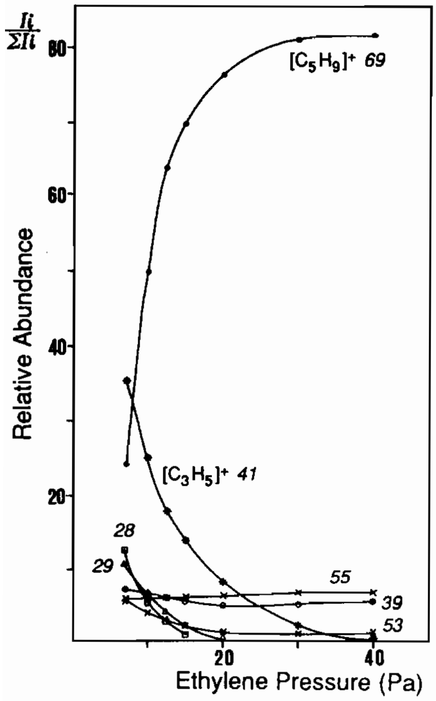


Fig. 4. Abundance vs. ethylene gas pressure for the ions of m/z: ● =69, × =55, χ=53, ∗ =41, ○=39, △=29, □=28.

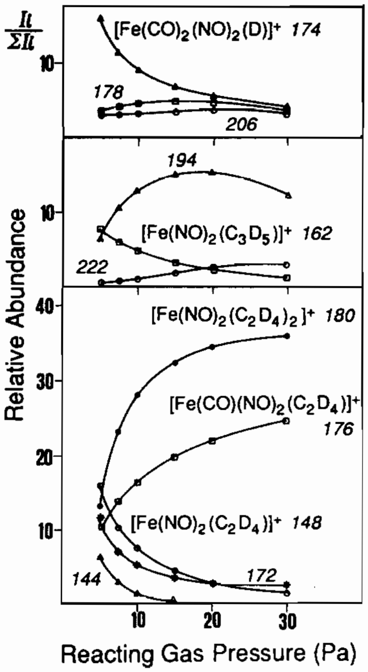
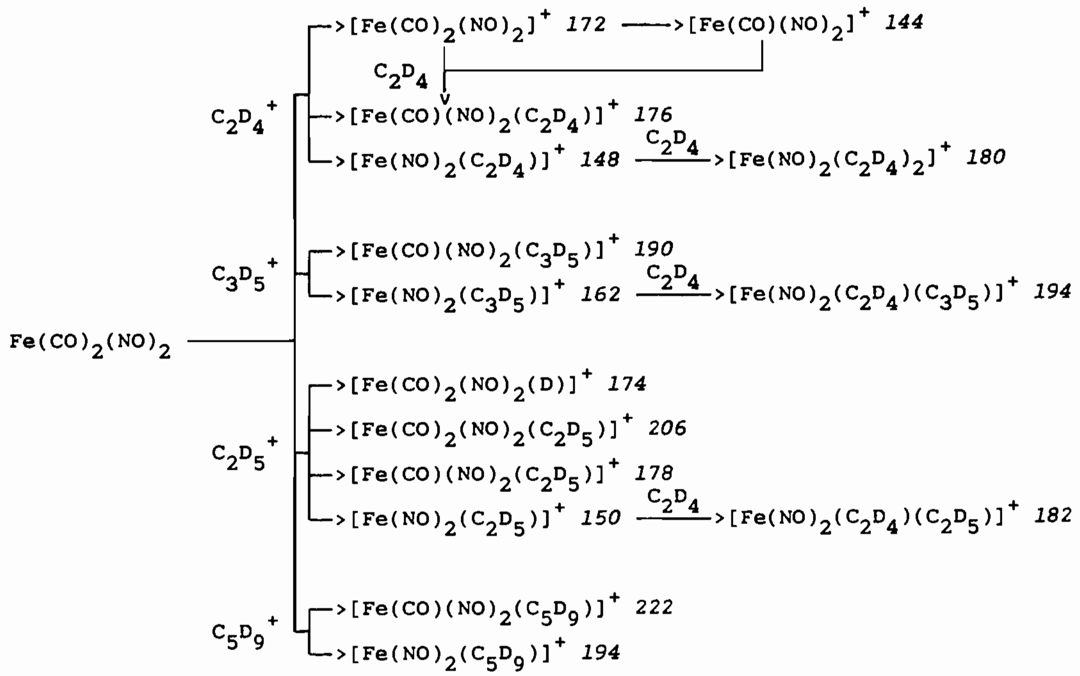


Fig. 5. Abundance vs. ethylene-d_4 gas pressure for selected ions of $Fe(CO)_2(NO)_2$; when not indicated, the ion formulae are reported in Scheme 2.

C_2D_4 with the formation of the 176 ion, which is formed via a CO substitution reaction from the ion 172 and, possibly, an addition reaction from the ion 144 which being coordinatively unsaturated, should be very reactive; correspondingly, the 176 ion increases remarkably with pressure.



Scheme 2.

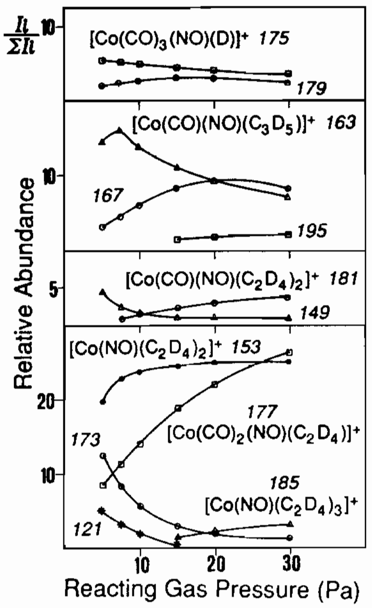


Fig. 6. Abundance vs. ethylene-d_4 gas pressure for selected ions of $Co(CO)_3(NO)$; when not indicated, the ion formulae are reported in Scheme 3.

The ability of this reactant system to give rise to carbonyl substitution and ethylene addition reactions is also evident from the nature of the ionic products. Among the more abundant ions is found $Fe(NO)_2(C_2D_4)_2^+$ ($m/z = 180$), which is formed by ethylene addition to the ion $Fe(NO)_2(C_2D_4)^+$ produced in a primary reaction with the loss of two carbonyl groups.

(b) Reactions with $C_3D_5^+$

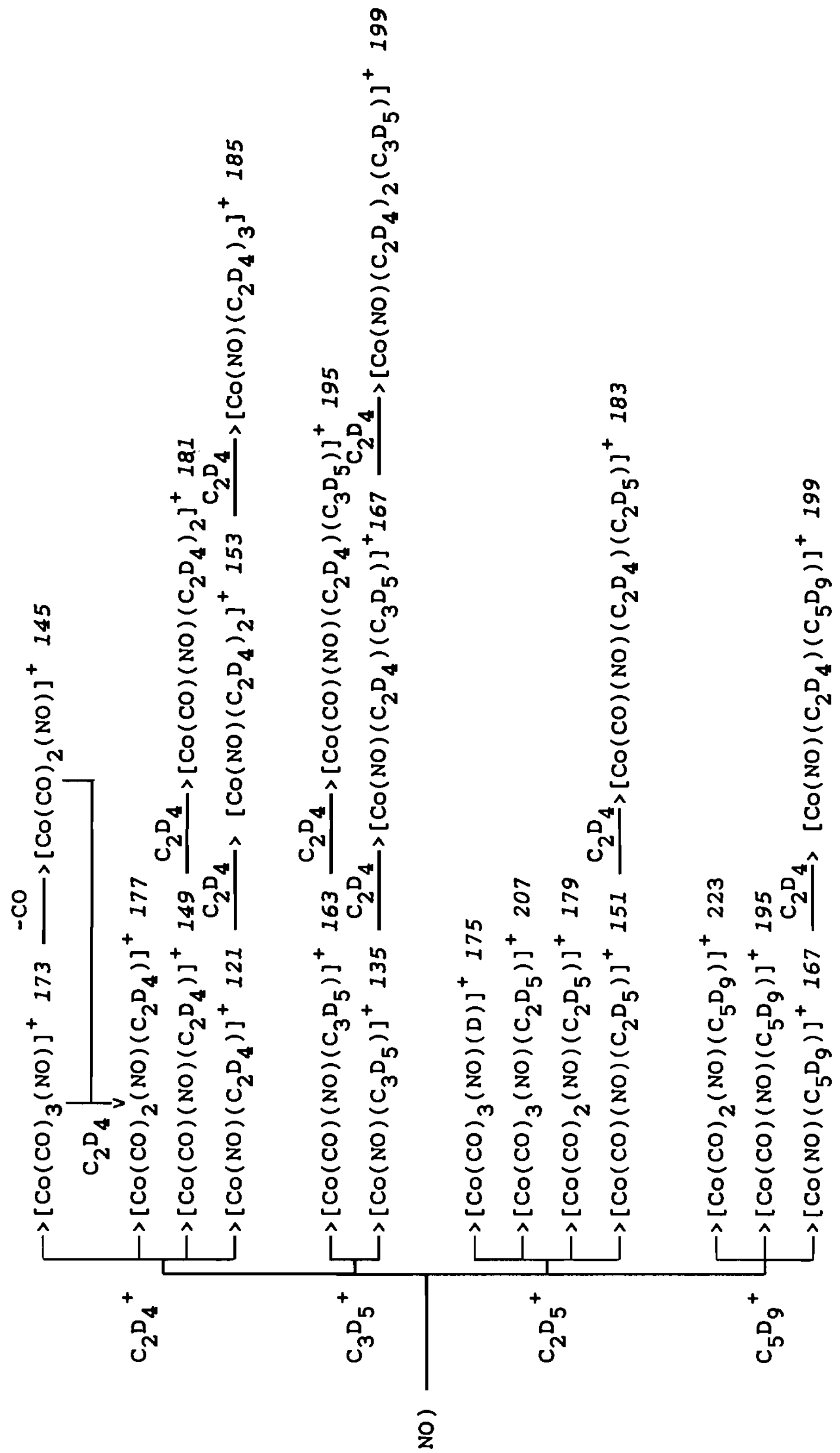
This ion gives rise to primary ions obtained by addition reactions accompanied by CO elimination (the loss of two CO groups is the preferred process); their abundance decreases as the reactant gas pressure increases for successive reactions with neutral C_2D_4; all these reactions end up with tetracoordinated ions.

(c) Reactions with $C_2D_5^+$

This ion gives rise to proton transfer and to addition reactions; these last reactions are accompanied by CO losses; the primary ions react, as usual, with neutral C_2D_4. The relative abundances of these ions are low and rather insensitive to the reactant gas pressure, so that the pathways leading to their formation are not identified.

(d) Reactions with $C_5D_9^+$

This ion gives rise to a CO substitution reaction forming a low abundance ion. A more important ion could be the 194 ion; an ion of the same mass is also formed in the reactions with $C_3D_5^+$. The increase of its abundance in the low pressure range suggests it is formed in the reactions promoted by $C_3D_5^+$, and the successive decrease in the high pressure range could be due to the decrease of the relative abundance of the $C_3D_5^+$ ion in the reactant


Co(CO)3(NO)
C2D4+
[Co(CO)3(NO)]+ 173
-CO
[Co(CO)2(NO)]+ 145
C2D4
[Co(CO)2(NO)(C2D4)]+ 177
[Co(CO)(NO)(C2D4)]+ 149
[Co(CO)(NO)(C2D4)2]+ 181
[Co(NO)(C2D4)]+ 121
[Co(NO)(C2D4)2]+ 153
[Co(NO)(C2D4)3]+ 185
C3D5+
[Co(CO)(NO)(C3D5)]+ 163
[Co(CO)(NO)(C2D4)(C3D5)]+ 195
[Co(NO)(C3D5)]+ 135
[Co(NO)(C2D4)(C3D5)]+ 167
[Co(NO)(C2D4)2(C3D5)]+ 199
C2D5+
[Co(CO)3(NO)(D)]+ 175
[Co(CO)3(NO)(C2D5)]+ 207
[Co(CO)2(NO)(C2D5)]+ 179
[Co(CO)(NO)(C2D5)]+ 151
[Co(CO)(NO)(C2D4)(C2D5)]+ 183
C5D9+
[Co(CO)2(NO)(C5D9)]+ 223
[Co(CO)(NO)(C5D9)]+ 195
[Co(NO)(C5D9)]+ 167
[Co(NO)(C2D4)(C5D9)]+ 199

Scheme 3.

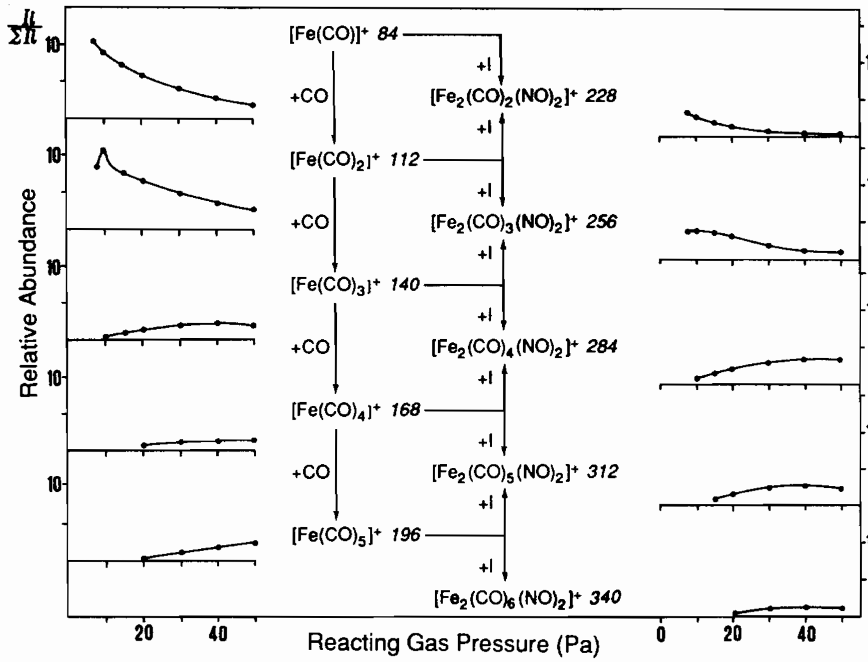


Fig. 7. Abundance vs. carbon monoxide gas pressure and reaction path of $Fe(CO)_2(NO)_2$; the primary ion is Fe(CO).

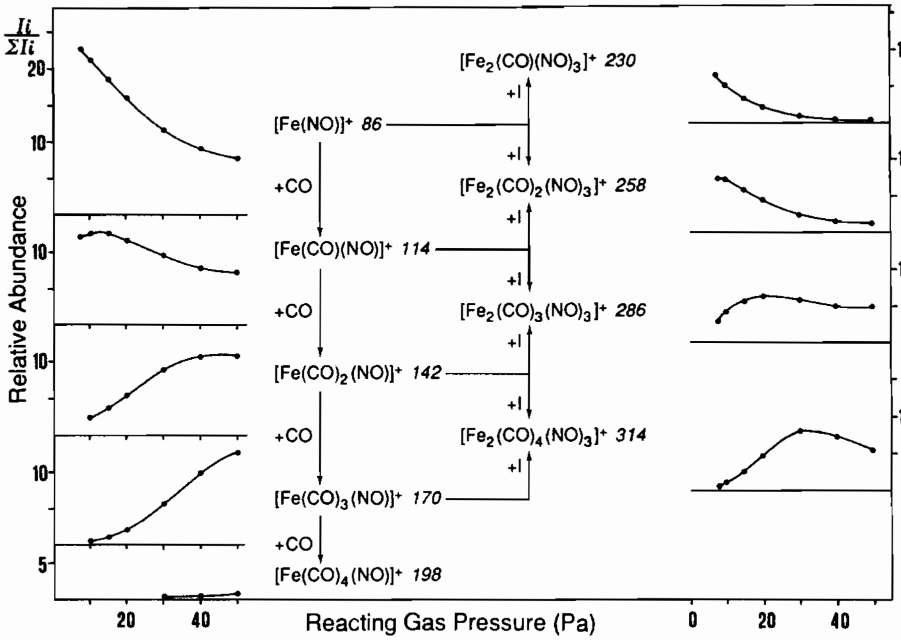


Fig. 8. Abundance vs. carbon monoxide gas pressure and reaction path of $Fe(CO)_2(NO)_2$; the primary ion is Fe(NO).

gas which is not offset by the corresponding increase of the $C_5D_9^+$ ion. This ion is therefore mainly due to the reactions promoted by $C_3D_5^+$, and only at rather high pressure could there be a contribution from the reaction of $C_5D_9^+$.

With this reacting system the major products are ions obtained by the loss of all the carbonyl groups, except for the 176 ion; a similar lability of the CO groups, already noted in gaseous phase for $Co(CO)_3NO$ [9a], is not found in solution.

Figure 6 shows the variation of the major ion abundances with the ethylene-d_4 pressure for compound **II**; the plots suggest a behaviour similar to that of compound **I**, and the proposed reaction Scheme 3 is not further discussed. However, we wish to point to some differences observed in comparison

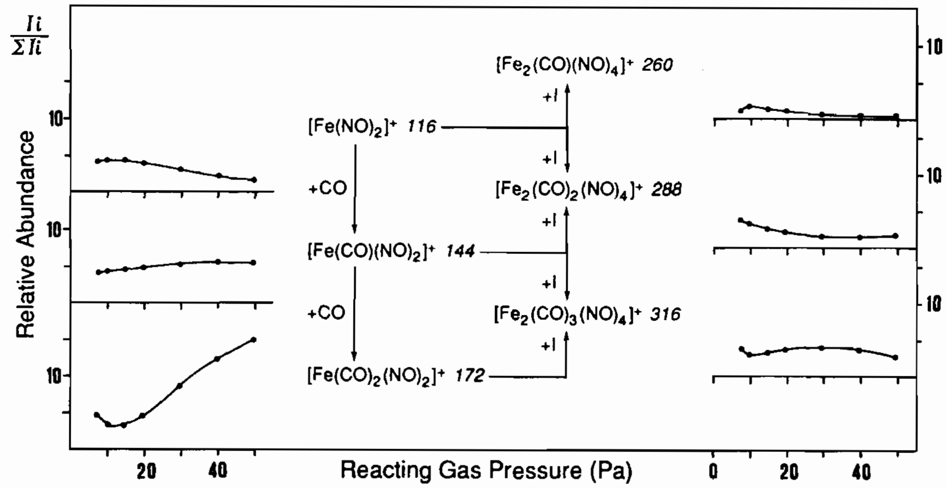


Fig. 9. Abundance vs. carbon monoxide gas pressure and reaction path of $Fe(CO)_2(NO)_2$; the primary ion is $Fe(NO)_2$.

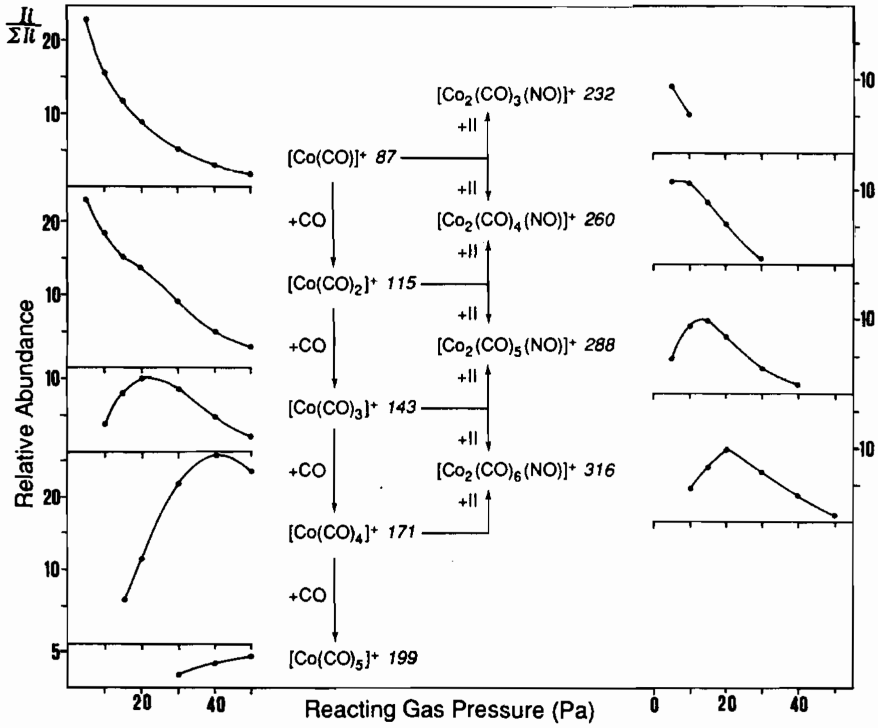


Fig. 10. Abundance vs. carbon monoxide gas pressure and reaction path of $Co(CO)_3(NO)$; the primary ion is $Co(CO)$.

with the ICR spectra, where addition reactions are not observed; in the CI spectra the ion $Co(CO)_2NO^+$ is able to add a neutral C_2D_4, as suggested by the continuous increase of the relative abundance of the 177 ion and the corresponding decrease of the ion 145; the reaction of $C_2D_4{}^+$ with $Co(CO)_3NO$ is also more complex, showing ions obtained by the loss of 1, 2 and 3 CO groups.

Carbon monoxide mass spectra

Carbon monoxide reacts by a charge exchange reaction with the transfer of a large amount of energy, giving rise to extensive fragmentation. Table 3 reports the mass spectra of **I** and **II**. For compound **I** the more abundant ions at low CO pressure are $Fe(CO)^+$, $Fe(CO)_2{}^+$, $Fe(CO)(NO)^+$ and $Fe(NO)^+$; these ions are probably formed in the first reaction along with smaller quantities of $Fe(NO)_2{}^+$; the molecular ion is also present at low CO pressure. Each of these fragment ions undergoes successive reactions with neutral CO according to the schemes reported in the Figs. 7–9.

The plots indicate that the CO pressure increase causes a decrease of some ions, while other ions

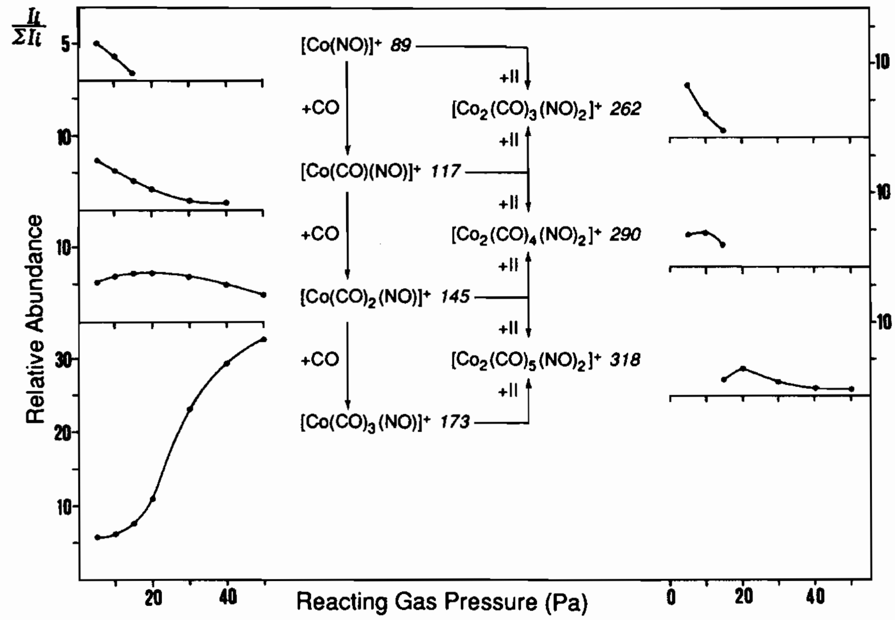


Fig. 11. Abundance vs. carbon monoxide gas pressure and reaction path of $Co(CO)_3(NO)$; the primary ion is Co(NO).

TABLE 3. Carbon monoxide chemical ionization mass spectra of iron and cobalt complexes

Ions	$Fe(CO)_2(NO)_2$	$Co(CO)_3(NO)$
$[M_2(CO)_6(NO)_2]^+$	10	
$[M_2(CO)_3(NO)_4]^+$	28	
$[M_2(CO)_4(NO)_3]^+$	58	
$[M_2(CO)_5(NO)_2]^+$	20	
$[M_2(CO)_6(NO)]^+$		11
$[M_2(CO)_2(NO)_4]^+$	14	
$[M_2(CO)_3(NO)_3]^+$	39	
$[M_2(CO)_4(NO)_2]^+$	20	
$[M_2(CO)_5(NO)]^+$		3
$[M_2(CO)(NO)_4]^+$	5	
$[M_2(CO)_2(NO)_3]^+$	16	
$[M_2(CO)_3(NO)_2]^+$	9	
$[M_2(CO)(NO)_3]^+$	5	
$[M_2(CO)_2(NO)_2]^+$	4	
$[M_2(CO)_2]^+$	18	
$[M(CO)_4(NO)]^+$	7	
$[M(CO)_5]^+$	14	9
$[M(CO)_2(NO)_2]^+$	100	
$[M(CO)_3(NO)]^+$	82	100
$[M(CO)_4]^+$	10	86
$[M(CO)(NO)_2]^+$	41	
$[M(CO)_2(NO)]^+$	82	15
$[M(CO)_3]^+$	17	24
$[M(NO)_2]^+$	17	
$[M(CO)(NO)]^+$	62	4
$[M(CO)_2]^+$	15	15
$[M(NO)]^+$	69	
$[M(CO)]^+$	19	11

M = metal atom.

TABLE 4. Ammonia chemical ionization mass spectra of iron and cobalt complexes

Ions	$Fe(CO)_2(NO)_2$	$Co(CO)_3(NO)$
$[M_2(NO)_2(NH_3)_3]^+$	18	
$[M_2(NO)(NH_3)_4]^+$	19	4
$[M_2(NO)(NH_3)_3]^+$		1
$[M(NO)_2(NH_3)_2]^+$	31	
$[M(NO)(NH_3)_3]^+$	100	100
$[M(NO)(NH_3)_2]^+$	7	7
$[M(NH_3)_3]^+$	30	58
$[M(NH_3)_2]^+$	17	15

M = metal atom.

TABLE 5. Nitrogen monoxide chemical ionization mass spectra of iron and cobalt complexes

Ions	$Fe(CO)_2(NO)_2$	$Co(CO)_3(NO)$
$[M_2-3CO+2NO]^+$	1	
$[M_2-2CO+NO]^+$	3	
$[M_2-CO]^+$	1	
$[M_2-3CO+NO]^+$		36
$[M_2-2CO]^+$	1	
$[M-2CO+2NO]^+$	33	15
$[M-CO+NO]^+$	100	97
$[M]^+$	16	5
$[M-3CO+2NO]^+$		100
$[M-2CO+NO]^+$	16	23
$[M-CO]^+$	1	23

M = molecular formula.

TABLE 6. Cluster ions observed in the nitrogen monoxide chemical ionization mass spectra of iron and cobalt complexes

m/z	Assignments	*I* (%)	*CVEN*
684	$[Co_6(NO)_{11}]^+$	2	86
654	$[Co_6(NO)_{10}]^+$	2	
565	$[Co_5(NO)_9]^+$	8	71
535	$[Co_5(NO)_8]^+$	3	
446	$[Co_4(NO)_7]^+$	37	56
387	$[Co_3(NO)_2]^+$	2	47
373	$[Co_3(NO)_5(NO_2)]^+$	12	
343	$[Co_3(NO)_4(NO_2)]^+$	3	
320	$[Co_2(CO)_4(NO)_3]^+$	5	
313	$[Co_3(NO)_3(NO_2)]^+$	3	
292	$[Co_2(CO)_3(NO)_3]^+$	100	32
268	$[Co_2(NO)_5]^+$	3	32
175	$[Co(CO)_2(NO)_2]^+$	53	17
149	$[Co(NO)_3]^+$	6	17
147	$[Co(CO)(NO)_2]^+$	3	16
902	$[Fe_7(NO)_{17}]^+$	3	106
872	$[Fe_7(NO)_{16}]^+$	5	103
842	$[Fe_7(NO)_{15}]^+$	6	100
812	$[Fe_7(NO)_{14}]^+$	3	97
786	$[Fe_6(NO)_{15}]^+$	13	92
756	$[Fe_6(NO)_{14}]^+$	39	89
726	$[Fe_6(NO)_{13}]^+$	10	86
696	$[Fe_6(NO)_{12}]^+$	7	83
670	$[Fe_5(NO)_{13}]^+$	14	78
640	$[Fe_5(NO)_{12}]^+$	13	75
610	$[Fe_5(NO)_{11}]^+$	8	72
580	$[Fe_5(NO)_{10}]^+$	6	69
550	$[Fe_5(NO)_9]^+$	2	66
520	$[Fe_5(NO)_8]^+$	1	63
490	$[Fe_5(NO)_7]^+$	1	60
460	$[Fe_5(NO)_6]^+$	26	57
554	$[Fe_4(NO)_{11}]^+$	2	64
434	$[Fe_4(NO)_7]^+$	11	61
438	$[Fe_3(NO)_9]^+$	8	50
408	$[Fe_3(NO)_8]^+$	3	47
378	$[Fe_3(NO)_7]^+$	15	44
348	$[Fe_3(NO)_6]^+$	4	41
322	$[Fe_2(NO)_7]^+$	8	37
262	$[Fe_2(NO)_5]^+$	3	30
232	$[Fe_2(NO)_4]^+$	4	28
202	$[Fe_2(NO)_3]^+$	4	26
318	$[Fe_2(CO)_2(NO)_5]^+$	84	34
290	$[Fe_2(CO)(NO)_5]^+$	70	32
316	$[Fe_2(CO)_3(NO)_4]^+$	28	33
288	$[Fe_2(CO)_2(NO)_4]^+$	19	31
174	$[Fe(CO)(NO)_3]^+$	100	18

CVEN = cluster valence electron number; the *CVENs* predicted according to the nuclearity of the cluster ions are: $M_2 = 34$, $M_3 = 48$, $M_4 = 60$, $M_5 = 72$, $M_6 = 86$ and $M_7 = 98$.

increase; the former are ions formed by the primary reactions, the others derive from the successive CO addition reactions. This general behaviour is illustrated by the ion $Fe(NO)^+$ (Fig. 8) whose abundance decreases constantly with the CO pressure while the abundance of its daughter ions is typical of a consecutive series. In this regard it is found that the ionic yield is almost constant for the series starting with $Fe(NO)^+$ and $Fe(CO)^+$, but an unexpected major increase is observed for the $Fe(CO)_2(NO)_2{}^+$ ion in the series starting with $Fe(NO)_2{}^+$, indicating that at high pressures an additional mechanism should be active for the formation of the 172 ion. Two possible ways can be conceived: the first one is a collision stabilization of the molecular ion formed in the primary charge exchange reaction, the second one is a charge exchange between the neutral iron compound and NO^+, which is an abundant ion in the CI mass spectra.

An increase of the coordination number is observed only when the total electron valence number does not exceed 18.

Rather abundant dimer ions are also observed; their relative abundance is related to that of the probable precursor as indicated in the Scheme. The addition to the ion source of more $Fe(CO)_2(NO)_2$ at a CO pressure of 50 Pa causes a sharp decrease of the monometallic ions, and a dramatic increase of the 314 ion; its low coordinative unsaturation [10] could be responsible for the stability of this ion.

Since the other primary ions (Figs. 7 and 9) behave in a similar way, their reactions are not further discussed; the sharp increase of the ion 316 after the addition of $Fe(CO)_2(NO)_2$ indicates again a high stability for this ion whose coordinative unsaturation is very low.

The results for compound II are plotted in Figs. 10 and 11; an analogous behaviour is evident and there is no need for further discussion.

Ammonia mass spectra

This reactant gas is unable to undergo charge exchange and proton transfer reactions. As reported in Table 4, the more representative ions are due to CO and/or NO substitution reactions; the unexpected metal-containing ions observed with this reacting gas could be due to a strong electrostatic interaction which strengthens the metal–ammonia bond.

Figures 12 and 13 show the variation of the major ion abundances with the ammonia pressure for compounds I and II; the plots indicate that the predominant products of the primary reactions correspond to the addition of $NH_3{}^+$ with ligand loss; the successive ammonia addition reactions, as indicated in Scheme 4, can be deduced from the plots of Figs. 12 and 13; it is also evident how the successive NH_3 additions occur with high efficiency, and the reactions proceed up to the addition of three NH_3 groups; if the final product is still coordinatively unsaturated

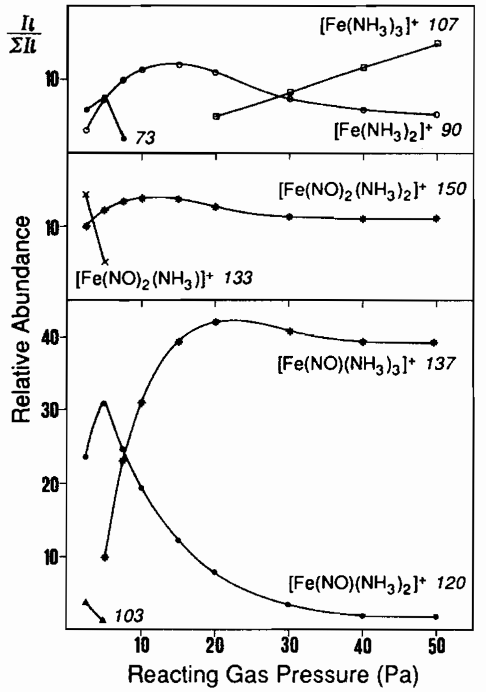


Fig. 12. Abundance vs. ammonia gas pressure for selected ions of $Fe(CO)_2(NO)_2$.

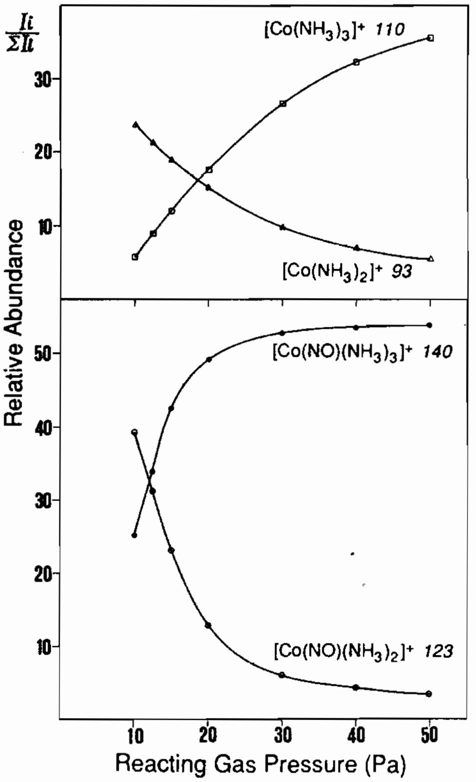


Fig. 13. Abundance vs. ammonia gas pressure for selected ions of $Co(CO)_3(NO)$.

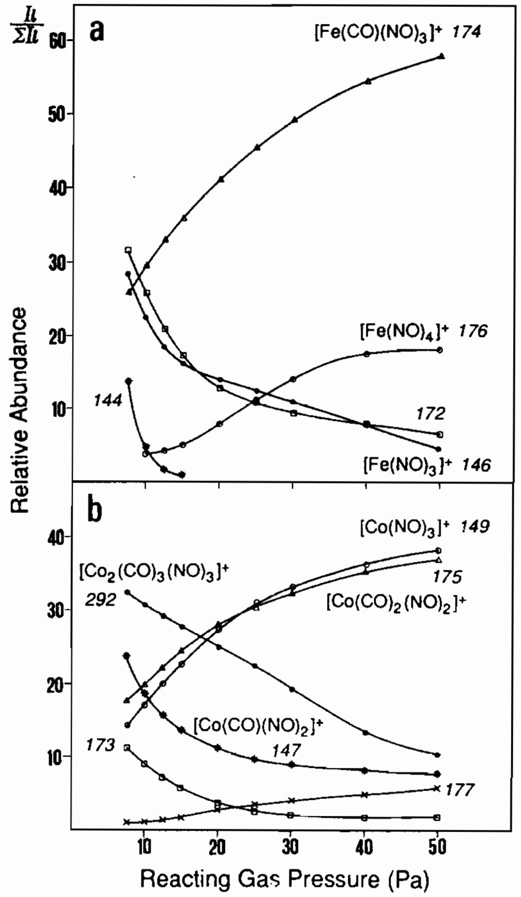


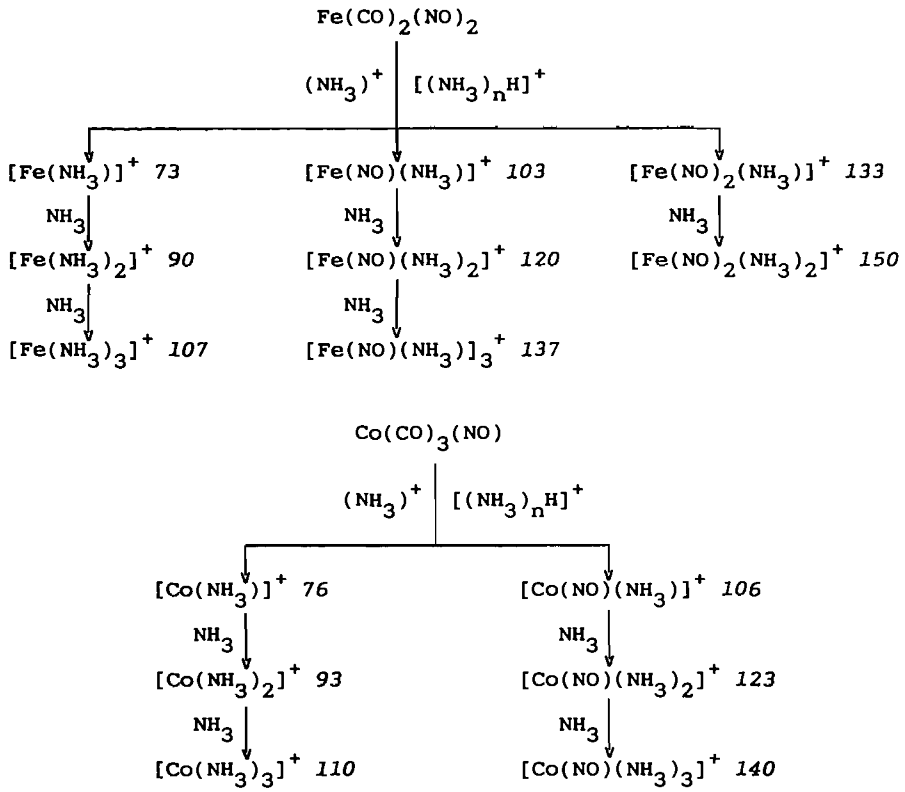
Fig. 14. Abundance vs. nitric monoxide gas pressure for selected ions of $Fe(CO)_2(NO)_2$ (a) and $Co(CO)_3(NO)$ (b).

$[Fe(NH_3)_3{}^+$ and $Co(NH_3)_3{}^+]$, it can further react with the neutral metal complex forming cluster ions.

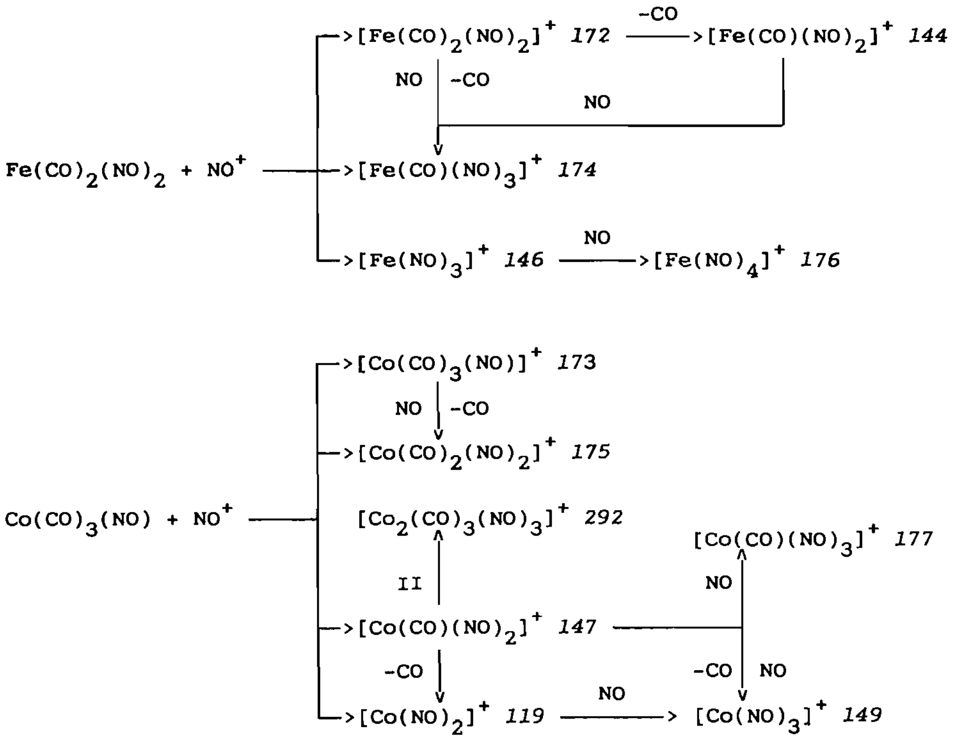
The one step displacement of three CO by $NH_3{}^+$ has already been reported [9a] for **II**; however, neither NO substitution nor addition of three NH_3 has been observed. While the failure of the ICR technique to observe the ion $[Co(NO)(NH_3)_3]^+$ may be attributable to the low ratio of ligand to metal complex pressure (2:1) previously used, the failure to observe ions obtained after the loss of NO groups indicates that the rate constants for these reactions should be substantially lower than those for the CO loss; only the high NH_3 concentration in the CI conditions makes these bimolecular reactions too fast to be observed in the mass spectrometer time scale.

Nitrogen monooxide mass spectra

NO^+ reacts with compound **I** with the formation of three ions: the molecular ion, formed by charge exchange and the ions $[Fe(CO)_n(NO)_3]^+$ ($n = 0$; 1) formed by NO^+ addition and CO loss. As shown in Fig. 14(a) the high relative abundance of these ions at low NO pressure indicates their formation



Scheme 4.



Scheme 5.

in primary reactions; of these ions only $[Fe(CO)(NO)_3]^+$ increases with the NO pressure, indicating (see Scheme 5) that it is also formed by reaction of neutral NO with metal containing ions; the sharp decrease of relative abundance of the 144 ion compared with that of the 172 ion should be due to its coordinative unsaturation; the formation of four coordinated species terminates the addition reactions. Relevant is the formation of the ion $[Fe(NO)_4]^+$, formally a 19 electron species, for which a different coordination mode of at least one nitrosyl group could be invoked. Table 5 reports the CI mass spectra of **I** and **II**.

A similar behaviour (Fig. 14(b) and Scheme 5) is also found for compound **II** whose NO addition/CO elimination reactions end with $Co(NO)_3{}^+$, a species already noted [11], as neutral molecule, in the gas phase reaction of **II** with NO.

Extensive clustering reactions are observed with this reagent gas; at low NO pressure dimer formation is noticed for compound **I**, while the ion $[Co_2(CO)_3(NO)_3]^+$ is one of the more abundant ions for compound **II**. An increase of the sample pressure causes a sharp decrease of the ions $[Co(NO)_3]^+$, $[Co(CO)(NO)_2]^+$ and a corresponding increase of the ion $[Co_2(CO)_3(NO)_3]^+$; the two former ions are thus able to react with the neutral molecule forming the dimer ion. The increase of the sample pressure also causes an extensive clustering in the two compounds, with preferential formation of NO containing ions. The observed ions are reported in Table 6 along with the *CVEN*s [12]. The variety of species and the observed *CVEN*s confirm the great aptitude of NO to act as ligand, adapting its coordination mode to allow an increase of the total coordination number.

Conclusions

The results described above indicate that CIMS is able to illuminate certain aspects of organometallic chemistry.

First of all this work clearly indicates that the ion formation pathways can be deduced by the influence exerted from the reacting gas pressure on the ion relative abundances. At low gas pressure it is possible to identify the ions conceived by a primary reaction, assuming that they are those with higher relative abundance; the knowledge of the thermochemistry of the involved reactions gives additional support in the identification of these primary ions. If, increasing the reactant gas pressure, a primary ion decreases, we can assume that it is consumed in one or more successive reactions; identification of these reactions is accomplished by observing which ions increase their abundance, or by allowing more substrate to reach the ion source.

This assertion is well supported by the behaviour of compounds **I** and **II** with CO as reagent gas. Moreover, preliminary data indicate that it is possible to reproduce with a good confidence the observed trends, assuming consecutive irreversible n-stage reactions with m initial substances [13]; the calculated rate constants fall in the range of 10^{-11}–10^{-12} cm^3 $molecules^{-1}$ s^{-1}, indicating that the reported reactions are usually facile and occur rapidly, having rate constants within an order of magnitude of the collision frequencies.

Our results confirm that there is a relationship between reactivity and coordinative unsaturation; in fact, in the higher pressure range the most intense ions are all nearly coordinatively saturated and do not show any tendency to further react, as their abundances are not appreciably influenced by the reacting gas pressure.

A second point of particular interest regards the different results obtained by ICR and by CI. ICR has proved to be a powerful technique for studying gas-phase ion-molecule reactions; nevertheless, the ICR normal experimental conditions (in particular the low ratio of gas to sample pressure) could prevent some reactions being observed. Our results clearly point out that unexpected reactions can occur if the experimental conditions allow them. This in contrast with the previous statements that in no case is the NO ligand displaced by another molecule and with the indication of the number of carbonyls displaced by the reacting gas [8a]. It is evident that in CI conditions even the C_2D_4 plays a significant role in carbonyl displacement reactions. These findings cast some caution in the use of scales based on the relative metal–ligand bond dissociation energies to predict reactions. The CI experimental conditions clearly point out that rich organometallic chemistry occurs in the gas phase, and we suggest using this technique as a rapid way to explore the reactivity of organometallic compounds; this should supply more help for synthetic inorganic chemistry.

The last point to notice is the role played by the NO ligand with regard to the reactivity. The extensive finding of pentacoordinated species strongly supports the hypothesis that the coordinated nitrosyl could change the mode of coordination favoring nucleophilic attack.

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